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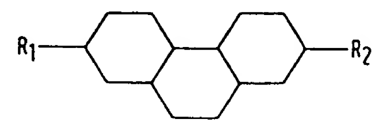
(54) Liquid crystal alkyl perhydrophenanthrenes

(57) Novel perhydrophenanthrene derivatives of the formula:



I

in which R_1 is alkyl having 1—10 C atoms, and R_2 is alkyl, alkoxy or alkanoyloxy having 1—10 C atoms, H, Br, Cl or CN, are suitable for us as components of liquid crystalline dielectrics.

The chemical formulae appearing in the printed specification were submitted after the date of filing, the formulae originally submitted being incapable of being satisfactorily reproduced.

SPECIFICATION

Perhydrophenanthrene derivatives, pr c sses for their preparation, and their us in liquid crystallin dielectrics and electr - ptical display elem nts

The present invention is concerned with certain novel perhydrophenanthrene derivatives, with processes for their preparation, and with their use in liquid crystalline dielectrics and electro-optical display elements.

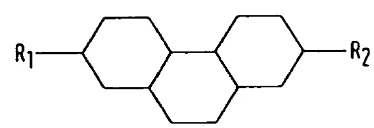
The properties of liquid crystalline materials of significantly varying their optical properties, such as light absorption, light scattering, birefringence, reflectivity or colour, under the influence of electric fields, are widely used in electro-optical display elements. Thus, the functioning of display elements of this type is based, for example, on the phenomena of dynamic scattering, the deformation of aligned phases, the Schadt-Helfrich effect in the twisted cell, or the cholesteric-nematic phase transition.

For the industrial application of these effects in electronic components, liquid crystalline dielectrics are required which must meet a large number of demands. The chemical resistance to moisture, air and physical influences, such as heat, radiation in the infra-red, visible and ultraviolet regions, and continuous and alternating electric fields, is of particular importance. Industrially usable liquid crystalline dielectrics are also required to have a liquid crystalline mesophase in the temperature range of from at least 0°C to +50°C, preferably from −10°C to 60°C, and the lowest possible viscosity at room temperature, which preferably should not exceed 50×10^{-3} Pa.s. Finally, they must not have any characteristic absorption in the region of visible light, that is to say they must be colourless.

A number of liquid crystalline compounds have been described which fulfill the stability demands made on dielectrics for electronic components and which are also colourless. However, no single compound has yet been described which fulfills all the requirements in respect of the range of temperature of the liquid crystalline mesophase, dielectric anisotropy, optical anisotropy, viscosity, specific resistance, and the shape of the electro-optical characteristic curve.

For this reason, mixtures are used, the composition of which is adapted to the particular requirements of each case. In order to vary the properties of the mixtures, as many different substances as possible are required, if possible from different classes of compounds in order to have sufficient scope in which to change the properties of the mixtures of substances. For this reason, there is a constant search for new liquid crystals with advantageous properties.

We have now found that perhydrophenanthrene derivatives of formula I:



I

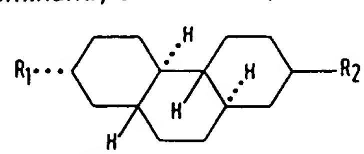
in which R_1 is alkyl having 1—10 C atoms and R_2 is alkyl, alkoxy or alkanoyloxy having 1—10 C atoms, H, Br, Cl or CN, are valuable components of liquid crystalline dielectrics. In particular, they have favourable clear points in the temperature range of from 50 to 120°C, and at the same time comparatively low melting points and an extremely low optical anisotropy in the region of about 0.02 to 0.06. They are therefore particularly suitable as components of liquid crystalline dielectrics for electro-optical display elements of the type described in German Patent Application 3,022,818, and also for improving the contrast in guest-host liquid crystal display elements. Furthermore, they have a negative anisotropy of diamagnetic susceptibility, which makes them suitable for use in electro-optical modulators of the type described in European Patent Specification 1 745.

The perhydrophenanthrene derivatives of formula I are novel and constitute one aspect of the present invention.

The present invention also comprises liquid crystalline dielectrics containing at least one perhydrophenanthrene derivative of formula I and electro-optical display elements comprising a liquid-crystal cell which contains a liquid crystalline dielectric according to the invention.

The compounds of formula I have several centres of asymmetry. Thus, on preparation, they can be obtained as racemates or, if optically active starting materials are used, in an optically active form. If mixtures of racemates are produced, the individual racemates can be isolated in a pure form from these, for example by re-crystallisation of the racemates themselves or of their diastereomeric derivatives, from inert solvents.

However, the synthesis is preferably carried out in such a manner that the preferred racemates of configuration Ia are formed either predominantly or exclusively:



Ia

in which the R_1 and R_2 substituents are equatorial.

Racemates obtained can be separated, if desired, into their optical antipodes either mechanically or chemically by known methods.

In the compounds of formula I, R_1 is an alkyl group having 1—10 C atoms, and thus is methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl or decyl. Those groups which contain 3 or more C atoms can be straight chain or branched; however, when an R_1 alkyl group has a branched chain, it is generally preferred that it contain not more than one chain branching. Of the branched alkyl groups, those in which a methyl or ethyl group is present in the 2- or 3-position on a relatively long carbon chain are preferred, such, for example, as 2- or 3-methylbutyl, 2- or 3-methylpentyl or 2- or 3-ethylhexyl.

Where the R_2 radical in the compounds of formula I also contains a carbon chain and is thus alkyl, alkoxy or alkanoyloxy, it is preferred that not more than one of the two radicals should contain a carbon chain which is branched not more than once. When R_2 is alkyl, alkoxy or alkanoyloxy, R_1 and R_2 together can contain 2 to 20 C atoms. Compounds of formula I are preferred in which R_1 and R_2 together contain 3—16, more preferably 4—14, C atoms. In the compounds of formula I wherein R_2 is hydrogen, Br, Cl or CN, R_1 preferably contains at least 2 or, more preferably, 3 or more C atoms.

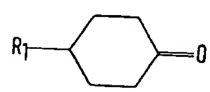
The present invention also comprises a process for the preparation of a perhydrophenanthrene derivative of the formula I specified above, which comprises reducing 7α-Butyl-2β-hexanoyloxyperhydrophenanthrene.

The foregoing processes can, in principle, be carried out in accordance with known procedures, as are described in the literature (for example in standard works, such as Houben-Weyl, *Methoden der Organischen Chemie* (Methods of Organic Chemistry), Georg-Thieme Verlag, Stuttgart; Organic Reactions, John Wiley & Sons, Inc., New York). Known variants of such procedures, which are not mentioned herein in detail, can also be used.

The starting materials can, if desired, be formed *in situ*, that is they are not isolated from the reaction mixture in which they are formed, but are immediately reacted further to give the compounds of formula I.

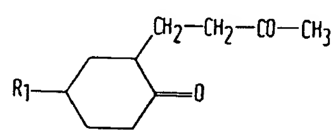
The starting materials of formulae II and III are new. They can be obtained, for example, as follows:

A cyclohexanone of formula IV:



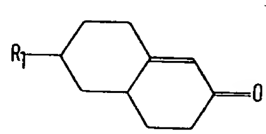
IV

is initially condensed in the presence of a base, for example morpholine, with methyl vinyl ketone to give a diketone of formula V:



V

This is then cyclised in the presence of an alkali metal hydroxide, for example NaOH, to give an octahydronaphthalene derivative of formula VI:

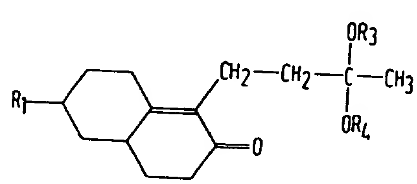


VI

A methyl ethyl ketone derivative of formula VII:

$$Z—CH_2—CH_2—\underset{OR_4}{\overset{OR_3}{C}}—CH_3 \qquad \text{VII}$$

in which Z is chlorine or bromine, and R_3 and R_4 are alkyl having 1—4 C atoms or together are alkylene having 2—4 C atoms, is then added on to VI in the presence of a strong base in a polar aprotic solvent, for example sodium dimethyl sulphoxide in dimethyl sulphoxide, to give a compound of formula VIII:



VIII

The double bond in the compound of formula VIII obtained is selectively reduced by a Birch reduction and, after splitting off the protective group by treatment with an alkali metal hydroxide, the reduction product is cyclised in an anhydrous organic solvent to give the ketone II.

The reduction of the unsaturated ketone II to give the saturated ketone III (X=O) or to give the alcohol III (X=H, OH) is preferably carried out in the manner of a Birch reduction with lithium in liquid ammonia. The saturated ketone III (X=O) can be converted, by reaction with an organometallic compound of the formula R'_2—M, preferably in an ether, such as diethyl ether, tetrahydrofuran (THF) or dioxane, and subsequent hydrolysis, splitting off water by acid treatment, for example with p-toluenesulphonic acid, and subsequent hydrogenation, into a compound of the formula I in which R_2 is alkyl.

The perhydrophenanthrene derivatives of formula I where in R_2 is H can be obtained either by subjecting the ketone III (X=O) to Wolff-Kishner reduction, or by splitting off water from the alcohol III (X=H, OH) in the presence of an acid, followed by hydrogenation of the unsaturated compound produced. Compounds of formula I wherein R_2 is an alkoxy group can be prepared from the alcohol III (X=H, OH) by etherification, for example by reaction with an alkyl halide in the presence of a base. The perhydrophenanthrene derivatives of formula I in which R_2 is an alkanoyloxy group can be prepared from the alcohol III (X=H, OH) by esterification with a carboxylic acid R''_2—COOH, wherein R''_2 is an alkyl group having 1—9 carbon atoms, or a reactive derivative thereof, for example a carbonyl chloride or carboxylic anhydride.

The compounds of formula I in which R_2 is Cl or Br, can be obtained from the alcohol III (X=H, OH) by treatment with a chlorinating or brominating agent, for example thionyl chloride or bromide.

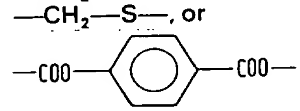
The preparation of the perhydrophenanthrene derivatives of formula I in which R_2 is CN is effected by reaction of the chlorine or bromine compounds with a cyanide, for example potassium cyanide or silver cyanide. Reactive esters of the alcohol III (X=H, OH), for example the tosylate, can also be used instead of the chlorine or bromine compounds I (R_2=Cl, Fr).

The dielectrics according to the invention comprise from 2 to 15, preferably 3 to 12, components, including at least one perhydrophenanthrene derivative of formula I. The other constituents are selected from the nematic or nematogenic compounds of the classes of azoxybenzenes, benzylideneanilines, biphenyls, terphenyls, phenyl or cyclohexyl benzoates, phenyl or cyclohexyl cyclohexanecarboxylates, phenylcyclohexanes, cyclohexylbiphenyls, cyclohexylcyclohexanes, cyclohexylnaphthalenes, 1,4-biscyclohexylbenzenes, 4,4′-bis-cyclohexylbiphenyls, phenylpyrimidines or cyclohexylpyrimidines, phenyldioxanes or cyclohexyldioxanes, stilbenes which may be halogenated, benzyl phenyl ethers, tolanes and substituted cinnamic acids. The most important compounds which can be used as constituents of liquid crystalline dielectrics of this type can be characterised by the formula IX:

$$R_5—(\mathrm{C})—B—(\mathrm{D})—R_6 \qquad \text{IX}$$

in which C and D are each a carbocyclic or heterocyclic ring system selected from 1,4-disubstituted benzene and cyclohexane rings, 4,4′-disubstituted biphenyl, phenylcyclohexane and cyclohexylcyclohexane systems, 2,5-disubstituted pyrimidine and 1,3-dioxane rings, 2,6-disubstituted naphthalene, dihydronaphthalene and tetrahydronaphthalene, quinazoline and tetrahydroquinazoline, B is

—CH=CH—
—CH=CY—
—C≡C—
—CO—O—
—CO—S—
—CH=N—
—N(O)=N—
—CH=N(O)—
—CH_2—CH_2—
—CH_2—O—
—CH_2—S—, or



or a C—C single bond, Y is halogen, preferably chlorine, or —CN, and R_5 and R_6 are alkyl, alkoxy, alkanoyloxy or alkoxycarbonyloxy having up to 18, preferably up to 8, C atoms, or one of these radicals is also —CN, —NC, —NO_2, —CF_3, F, Cl or Br. In most of these compounds, R_5 and R_6 are different, from one another, one of these radicals preferably being an alkyl or alkoxy group. Other variants of the envisaged substituents, however, are also common. Many such substances, and also mixtures thereof, are commercially available.

The dielectrics according to the invention generally contain at least 30, preferably 50—99, and more preferably 60—98, % by weight of the compounds of formulae I and IX. Of this, preferably at least 5% by weight, and more preferably 10—40% by weight, is made up of one or more compounds of formula I. The invention also comprises those liquid crystalline dielectrics to which less than 5% by weight, for example 0.1 to 3% by weight, of one or more compounds of formula I is present, for example for doping purposes. On the other hand, the compounds of formula I can account for up to

60% by weight of the dielectrics according to the invention. The liquid crystalline dielectrics according to the invention preferably contain 10 to 30% by weight of one or more compounds of formula I.

The preparation of the diel ctrics according to the invention may be carried out in conventional manner. The desired amount of the compounds used in a smaller quantity is preferably dissolved in the component constituting the major constituent, advantageously at an elevated temperature. If a temperature above the clear point of the major constituent is chosen for this, the completeness of the solution process can be observed with particular ease.

The liquid crystalline dielectrics according to the invention can be modified by suitable additives in such a way that they can be used in all hitherto disclosed types of liquid crystal display elements. Suitable additives for this purpose are known to those skilled in the art and are extensively described in the relevant literature. Suitable additives include, for example, dichroic dyes and compounds which are intended to modify the dielectric anisotropy, viscosity, conductivity and/or orientation of the nematic phases. Additives of these kinds are described, for example, in German OLS 2,209,127, 2,240,864, 2,321,632, 2,338,281, 2,450,088, 2,637,430, 2,853,728 and 2,902,177.

In order that the invention may be more fully understood, the following Examples are given by way of illustration. In these Examples, m.p. denotes the melting point, and c.p. denotes the clear point of a liquid crystalline substance; b.p. denotes boiling point. All temperatures are in °C; unless otherwise stated, parts or percentages are by weight. "Usual working up" means that water is added, if necessary, to the reaction mixture, the latter is extracted with ether, the extract is separated, the organic phase is dried over sodium sulphate, filtered, evaporated and purified, where appropriate, by column chromatography (the absorbent and the eluant are indicated in brackets).

In the following Examples, 4aβ, 4bα, 8aβ, 10aα-perhydrophenanthrene is abbreviated to "perhydrophenanthrene".

Preparation Examples:

Example 1

A solution of 2.9 g of 7α-hexyl-2β-perhydrophenanthrenol (m.p. 126°; obtained by reaction of 4-hexylcyclohexanone with morpholine to give 4-n-hexyl-1-morpholino-1-cyclohexene (b.p. 143°/0.01 Torr), reaction with methyl vinyl ketone to give 4-hexyl-2-(3-oxobutyl)cyclohexanone (b.p. 158°/0.02 Torr), cyclisation to give 6α-hexyl-2,3,4,4aβ,5,6,7,8-octahydro-2-naphthalenone (b.p. 136—140°/1.5 Torr), reaction with 1-bromo-3,3-ethylenedioxybutane to give 1-(3,3-ethylenedioxybutyl)-6α-hexyl-2,3,4,4aβ,5,6-7,8-octahydro-2-naphthalenone, reduction with Li/NH_3 to give 1α-(3,3-ethylenedioxybutyl)-6α-hexyl-4aβ,8aα-decahydro-2-naphthalenone, ketal cleavage and cyclisation to give 7α-hexyl-4aβ,4bα,8aβ-dodecahydro-2-phenanthenone (m.p. 77°), Birch reduction to give 7-hexylperhydro-2-phenanthrenone (m.p. 49°) and further Birch reduction after the addition of methanol) and 0.3 g of p-toluenesulphonic acid in 30 ml of toluene was boiled under a water separator for 2 hours. The mixture was allowed to cool down, filtered through Al_2O_3 and evaporated. The residue was hydrogenated in 30 ml of THF on 0.5 g of 5% Pd-C at 60° and 6 bar until no further change. After filtration and evaporation, 7α-hexylperhydrophenanthrene was obtained.

Examples 2 to 10

Using the process of Example 1, the following compounds are obtained from the corresponding 4-R_1-cyclohexanones via the corresponding 7α-R_1-perhydro-2-phenanthrenones and 7α-R_1-perhydro-2-phenanthrenols:

2. 7α-Methylperhydrophenanthrene.
3. 7α-Ethylperhydrophenanthrene.
4. 7α-Propylperhydrophenanthrene.
5. 7α-Butylperhydrophenanthrene.
6. 7α-Pentylperhydrophenanthrene.
7. 7α-Heptylperhydrophenanthrene.
8. 7α-Octylperhydrophenanthrene.
9. 7α-Nonylperhydrophenanthrene.
10. 7α-Decylperhydrophenanthrene.

Example 11

A solution of 145 g of 7α-hexylperhydro-2-phenanthrenone in 200 ml of ether was added dropwise to a Grignard solution prepared from 85 g of hexyl bromide and 13 g of magnesium in 400 ml of ether, with stirring and cooling. After boiling for one hour, the mixture was poured on to dilute hydrochloric acid/ice, extracted several times with ether, the extracts were washed to neutrality, dried over sodium sulphate and evaporated. The crude mixture of 2α,7α-dihexyl-2β-perhydrophenanthrenol and 2β,7α-dihexyl-2α-perhydrophenanthrenol obtained was dissolved in 400 ml of toluene. After adding 10 g of p-toluenesulphonic acid, the mixture was boiled for 3 hours under a water separator, allowed to cool, filtered through Al_2O_3 and evaporated. The crude mixture of 2,7α-dihexyldodecahydrophenanthrenes was hydrogenated in 1 l of tetrahydrofuran and in the presence of 50 g of 5% Pd-C at 60° and 6 bar until no further change. After filtration and evaporation, a mixture of 2α,7α- and 2β,7α-dihexylperhydrophenanthrene was obtained, which can be separated by HPLC.

Examples 12 to 20

Using the process of Example 11, the following compounds are obtained from the corresponding 7α-R_1-perhydro-2-phenanthrenones:

12. 2α,7α- and 2β,7α-Dimethylperhydroph nanthrenone.
13. 2α,7α- and 2β,7α-Diethylperhydrophenanthrene.
14. 2α, 7α- and 2β,7α-Dipropylperhydrophenanthrene.
15. 2α,7α- and 2β,7α-Dibutylperhydrophenanthrene.
16. 2α,7α- and 2β,7α-Dipentylperhydrophenanthrene.
17. 2α,7α- and 2β,7α-Diheptylperhydrophenanthrene.
18. 2α,7α- and 2β,7α-Dioctylperhydrophenanthrene.
19. 2α,7α- and 2β,7α-Dinonylperhydrophenanthrene.
20. 2α,7α- and 2β,7α-Didecylperhydrophenanthrene.

Example 21

30 mg of a 55% NaH dispersion were added to a solution of 150 mg of 7α-hexyl-2β-perhydrophenanthrenol in 25 ml of THF and the mixture was stirred for one hour under N_2. A solution of 100 mg of n-bromopentane in 5 ml of THF was then added and the mixture was boiled overnight with stirring. After cooling down, the precipitated salts were removed by filtration, the filtrate was evaporated and the residue was chromatographed (silica gel 60; petroleum ether: ether=95:5). 7α-Hexyl-2β-pentyloxyperhydrophenanthrene was obtained, m.p. 55°, c.p. 64° (from methanol).

Examples 22 to 50

Using the process of Example 21, the following compounds are obtained by etherification:

22. 7α-Ethyl-2β-propyloxyperhydrophenanthrene.
23. 2β-Butyloxy-7α-ethylperhydrophenanthrene.
24. 7α-Ethyl-2β-pentyloxyperhydrophenanthrene.
25. 7α-Ethyl-2β-hexyloxyperhydrophenanthrene.
26. 7α-Ethyl-2β-heptyloxyperhydrophenanthrene.
27. 7α-Propyl-2β-propyloxyperhydrophenanthrene.
28. 2β-Butyloxy-7α-propylperhydrophenanthrene.
29. 2β-Pentyloxy-7α-propylperhydrophenanthrene.
30. 2β-Hexyloxy-7α-propylperhydrophenanthrene.
31. 2β-Heptyloxy-7α-propylperhydrophenanthrene.
32. 7α-Butyl-2β-propyloxyperhydrophenanthrene.
33. 7α-Butyl-2β-butyloxyperhydrophenanthrene.
34. 7α-Butyl-2β-pentyloxyperhydrophenanthrene.
35. 7α-Butyl-2β-hexyloxyperhydrophenanthrene.
36. 7α-Butyl-2β-heptyloxyperhydrophenanthrene.
37. 7α-Pentyl-2β-propyloxyperhydrophenanthrene.
38. 2β-Butyloxy-7α-pentylperhydrophenanthrene.
39. 7α-Pentyl-2β-pentyloxyperhydrophenanthrene.
40. 2β-Hexyloxy-7α-pentylperhydrophenanthrene.
41. 2β-Heptyloxy-7α-pentylperhydrophenanthrene.
42. 7α-Hexyl-2β-propyloxyperhydrophenanthrene.
43. 2β-Butyloxy-7α-hexylperhydrophenanthrene.
44. 7α-Hexyl-2β-hexyloxyperhydrophenanthrene.
45. 7α-Hexyl-2β-heptyloxyperhydrophenanthrene.
46. 7α-Heptyl-2β-propyloxyperhydrophenanthrene.
47. 2β-Butyloxy-7α-heptylperhydrophenanthrene.
48. 7α-Heptyl-2β-pentyloxyperhydrophenanthrene.
49. 2β-Hexyloxy-7α-heptylperhydrophenanthrene.
50. 7α-Heptyl-2β-heptyloxyperhydrophenanthrene.

Example 51

About 50 mg of hexanoyl chloride were added dropwise to a solution of 60 mg of 7α-hexyl-2β-perhydrophenanthrenol in 2 ml of pyridine and the mixture was stirred overnight, and then poured onto ice. After the usual working up (silica gel); petroleum ether: CH_2Cl_2: ether=5.0:3.5:1.5), 2β-hexanoyloxy-7α-hexylperhydrophenanthrene was obtained, m.p. 57°, c.p. 76° (from ethanol).

Examples 52 t 103

Using the process of Example 51, the following compounds are obtained from the corresponding alcohols with the appropriate acid chlorides:

52. 2β-Acetoxy-7α-propylperhydrophenanthrene.
53. 2β-Acetoxy-7α-butylperhydrophenanthrene.
54. 2β-Acetoxy-7α-pentylperhydrophenanthrene.

55. 2β-Acetoxy-7α-hexylperhydrophenanthrene, m.p. 74°, c.p. 65° (monotropic).
56. 2β-Acetoxy-7α-heptylperhydrophenanthrene.
57. 2β-Propionyloxy-7α-propylperhydrophenanthrene.
58. 7α-Butyl-2β-propionyloxyperhydrophenanthrene.
59. 7α-Pentyl-2β-propionyloxyperhydrophenanthrene.
60. 7α-Hexyl-2β-propionyloxyperhydrophenanthrene, m.p. 73°, c.p. 85°.
61. 7α-Heptyl-2β-propionyloxyperhydrophenanthrene.
62. 2β-Butyryloxy-7α-propylperhydrophenanthrene.
63. 7α-Butyl-2β-butyryloxyperhydrophenanthrene.
64. 2β-Butyryloxy-7α-pentylperhydrophenanthrene.
65. 2β-Butyryloxy-7α-hexylperhydrophenanthrene, m.p. 53°, c.p. 82°.
66. 2β-Butyryloxy-7α-heptylperhydrophenanthrene.
67. 2β-Pentanoyloxy-7α-propylperhydrophenanthrene.
68. 7α-Butyl-2β-pentanoyloxyperhydrophenanthrene.
69. 2β-Pentanoyloxy-7α-pentylperhydrophenanthrene.
70. 7α-Hexyl-2β-pentanoyloxyperhydrophenanthrene, m.p. 57°, c.p. 76°.
71. 7α-Heptyl-2β-pentanoyloxyperhydrophenanthrene.
72. 2β-Hexanoyloxy-7α-propylperhydrophenanthrene.
73. 7α-Butyl-2β-hexanoyloxyperhydrophenanthrene, m.p. 68°, c.p. 60° (monotropic).
74. 2β-Hexanoyloxy-7α-pentylperhydrophenanthrene, m.p. 70°, c.p. 78°.
75. 7α-Heptyl-2β-hexanoyloxyperhydrophenanthrene, m.p. 66°, c.p. 80°.
76. 2β-Hexanoyloxy-7α-octylperhydrophenanthrene, m.p. 57°, c.p. 79°.
77. 2β-Hexanoyloxy-7α-nonylperhydrophenanthrene.
78. 7α-Decyl-2β-hexanoyloxyperhydrophenanthrene, m.p. 65°, c.p. 78°.
79. 2β-Heptanoyloxy-7α-propylperhydrophenanthrene.
80. 7α-Butyl-2β-heptanoyloxyperhydrophenanthrene.
81. 2β-Heptanoyloxy-7α-pentylperhydrophenanthrene.
82. 2β-Heptanoyloxy-7α-hexylperhydrophenanthrene, m.p. 59°, c.p. 73°.
83. 2β-Heptanoyloxy-7α-octylperhydrophenanthrene.
84. 2β-Octanoyloxy-7α-propylperhydrophenanthrene.
85. 7α-Butyl-2β-octanoyloxyperhydrophenanthrene.
86. 2β-Octanoyloxy-7α-pentylperhydrophenanthrene.
87. 7α-Hexyl-2β-octanoyloxyperhydrophenanthrene, m.p. 69°, c.p. 68° (monotropic).
88. 7α-Heptyl-2β-octanoyloxyperhydrophenanthrene.
89. 2β-Octanoyloxy-7α-octylperhydrophenanthrene.
90. 2β-Nonanoyloxy-7α-propylperhydrophenanthrene.
91. 7α-Butyl-2β-nonanoyloxyperhydrophenanthrene.
92. 2β-Nonanoyloxy-7α-pentylperhydrophenanthrene.
93. 7α-Hexyl-2β-nonanoyloxyperhydrophenanthrene, m.p. 68°, c.p. 72°.
94. 7α-Heptyl-2β-nonanoyloxyperhydrophenanthrene.
95. 2β-Nonanoyloxy-7α-octylperhydrophenanthrene.
96. 2β-Decanoyloxy-7α-propylperhydrophenanthrene.
97. 7α-Butyl-2β-decanoyloxyperhydrophenanthrene.
98. 2β-Decanoyloxy-7α-pentylperhydrophenanthrene.
99. 2β-Decanoyloxy-7α-hexylperhydrophenanthrene, m.p. 70°, c.p. 72°.
100. 2β-Decanoyloxy-7α-heptylperhydrophenanthrene.
101. 2β-Decanoyloxy-7α-octylperhydrophenanthrene.
102. 2β-Decanoyloxy-7α-nonylperhydrophenanthrene.
103. 2β-Decanoyloxy-7α-decylperhydrophenanthrene.

Example 104

A solution of 1.74 g of triphenylphosphine in 5 ml of THF was added dropwise under nitrogen to a solution of 1.19 g of N-bromosuccinimide in 5 ml of THF. To this was added a solution of 7α-hexyl-2α-perhydrophenanthrenol (obtained from 7α-hexylperhydro-2-phenanthrenone and potassium tris-sec.-butylborohydride in THF) in 5 ml of THF. The mixture was boiled for 4 hours, then further stirred overnight at 20° and the reaction mixture was subjected to usual working up (silica gel 60; n-hexane). 2β-Bromo-7α-hexylperhydrophenanthrene was obtained, m.p. 92° (from acetone).

Examples 105 to 123

Using the process of Example 104, the following compounds are obtained from the corresponding alcohols with N-chlorosuccinimide or N-bromosuccinimide:

105. 2β-Chloro-7α-methylperhydrophenanthrene.
106. 2β-Chloro-7α-ethylperhydrophenanthrene.
107. 2β-Chloro-7α-propylperhydrophenanthrene.
108. 7α-Butyl-2β-chlorop rhydrophenanthrene.

109. 2β-Chloro-7α-pentylperhydrophenanthrene.
110. 2β-Chloro-7α-hexylperhydrophenanthrene.
111. 2β-Chloro-7α-heptylperhydrophenanthrene.
112. 2β-Chloro-7α-octylperhydrophenanthrene.
113. 2β-Chloro-7α-nonylperhydrophenanthrene.
114. 2β-Chloro-7α-decylperhydrophenanthrene.
115. 2β-Bromo-7α-methylperhydrophenanthrene.
116. 2β-Bromo-7α-ethylperhydrophenanthrene.
117. 2β-Bromo-7α-propylperhydrophenanthrene.
118. 2β-Bromo-7α-butylperhydrophenanthrene.
119. 2β-Bromo-7α-pentylperhydrophenanthrene.
120. 2β-Bromo-7α-heptylperhydrophenanthrene.
121. 2β-Bromo-7α-octylperhydrophenanthrene.
122. 2β-Bromo-7α-nonylperhydrophenanthrene.
123. 2β-Bromo-7α-decylperhydrophenanthrene.

Example 124

A solution of 410 mg of 7α-hexyl-2β-p-toluenesulfonyloxyperhydrophenanthrene (m.p. 71°) and 724 mg of sodium cyanide in 50 ml of N-methylpyrrolidone was stirred at 90° for 20 hours. After cooling, the mixture was diluted with water and subjected to usual working up (silica gel 60; petroleum ether:ether=95:5). 2β-Cyano-7α-hexylperhydrophenanthrene was obtained, m.p. 89°, c.p. 91°.

Examples 125 to 134

Using the process of Example 124, the following compounds are obtained from the corresponding chlorides, bromides or p-toluenesulfonates with NaCN:

125. 2β-Cyano-7α-methylperhydrophenanthrene.
126. 2β-Cyano-7α-ethylperhydrophenanthrene.
127. 2β-Cyano-7α-propylperhydrophenanthrene.
128. 7α-Butyl-2β-cyanoperhydrophenanthrene.
129. 2β-Cyano-7α-pentylperhydrophenanthrene.
130. 2β-Cyano-7α-hexylperhydrophenanthrene.
131. 2β-Cyano-7α-heptylperhydrophenanthrene.
132. 2β-Cyano-7α-octylperhydrophenanthrene.
133. 2β-Cyano-7α-nonylperhydrophenanthrene.
134. 2β-Cyano-7α-decylperhydrophenanthrene.

The following Examples relate to mixtures of compounds of formula I with one another or with other liquid crystalline substances which can be used as dielectrics according to the invention.

Example A

A mixture of
18% of 7α-butyl-2β-hexanoyloxyperhydrophenanthrene,
17% of 2β-hexanoyloxy-7α-pentylperhydrophenanthrene,
23% of 2β-hexanoyloxy-7α-hexylperhydrophenanthrene,
20% of 7α-heptyl-2β-hexanoyloxyperhydrophenanthrene,
and
22% of 7α-decyl-2β-hexanoyloxyperhydrophenanthrene,
has the following characteristics: m.p. 5°, c.p. 75°, viscosity 41 $mm^2.sec^{-1}$ at 20°, dielectric anisotropy −0.5, optical anisotropy +0.05.

Example B

A mixture of
10% of 7α-butyl-2β-hexanoyloxyperhydrophenanthrene,
10% of 2β-hexanoyloxy-7α-pentylperhydrophenanthrene,
13% of 2β-hexanoyloxy-7α-hexylperhydrophenanthrene,
11% of 7α-heptyl-2β-hexanoyloxyperhydrophenanthrene,
25% of trans,trans-4-ethylcyclohexylcyclohexane-4′-carbonitrile,
4% of trans,trans-4-propylcyclohexylcyclohexane-4′-carbonitrile,
23% of trans,trans-4-butylcyclohexylcyclohexane-4′-carbonitrile, and
4% of trans,trans-4-pentylcyclohexylcyclohexane-4′-carbonitrile
has the following characteristics: m.p. −20°, c.p. 68°, viscosity 56 $mm^2.sec^{-1}$ at 20°, dielectric anisotropy +2.3, optical anisotropy +0.057.

Example C

A mixture of
9% of 7α-butyl-2β-hexanoyloxyperhydrophenanthrene,
9% of 2β-hexanoyloxy-7α-pentylperhydrophenanthrene,

13% of 2β-hexanoyloxy-7α-hexylperhydrophenanthrene,
11% of 7α-heptyl-2β-hexanoyloxyperhydrophenanthrene,
25% of trans,trans-4-ethylcyclohexylcyclohexane-4'-carbonitrile,
23% of trans,trans-4-butylcyclohexylcyclohexane-4'-carbonitrile, and
10% of trans-4-propylcyclohexyl trans,trans-4-butylcyclohexylcyclohexane-4'-carboxylate

has the following characteristics: m.p. −5°, c.p. 77°, viscosity 52 $mm^2.sec^{-1}$, dielectric anisotropy +2, optical anisotropy +0.056.

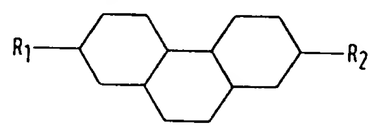
Example D

A mixture of
18% of 4-(trans-4-pentylcyclohexyl)benzonitrile,
13% of 2β-hexanoyloxy-7α-hexylperhydrophenanthrene,
11% of 7α-heptyl-2β-hexanoyloxyperhydrophenanthrene,
25% of trans,trans-4-ethylcyclohexylcyclohexane-4'-carbonitrile,
23% of trans,trans-4-butylcyclohexylcyclohexane-4'-carbonitrile, and
10% of trans-4-propylcyclohexyl trans,trans-4-butylcyclohexylcyclohexane-4'-carboxylate

has the following characteristics: m.p. −6°, c.p. 74°, viscosity 47 $mm^2.sec^{-1}$, dielectric anisotropy +3.8, optical anisotropy +0.07.

Claims

1. Perhydrophenanthrene derivatives of formula I:



I

in which R_1 is alkyl having 1—10 C atoms, and R_2 is alkyl, alkoxy or alkanoyloxy having 1—10 C atoms, H, Br, Cl or CN.

2. Perhydrophenanthrene derivatives according to Claim 1, in which R is alkyl, alkoxy or alkanoyloxy and R_1 and R_2 together contain 4—14 C atoms.

3. 7α-Butyl-2β-hexanoyloxyperhydrophenanthrene.

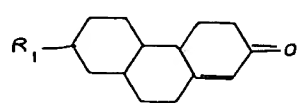
4. 2β-Hexanoyloxy-7α-pentylperhydrophenanthrene.

5. 2β-Hexanoyloxy-7α-hexylperhydrophenanthrene.

6. 7α-Heptyl-2β-hexanoyloxyperhydrophenanthrene.

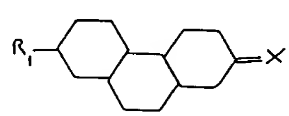
7. 7α-Decyl-2β-hexanoyloxyperhydrophenanthrene.

8. A process for the preparation of a perhydrophenanthrene derivative of formula I specified in Claim 1, which comprises reducing a ketone of formula II:



II

in which R_1 has the meaning specified in Claim 1, to form a compound of formula III:



III

in which X is O or (H, OH), and, when X is O, reacting the compound of formula III with a compound of the formula R'_2—M, in which R'_2 is alkyl having 1—10 C atoms, M is Li or MgHal, and Hal is chlorine, bromine or iodine, and successively hydrolysing, splitting off water from, and hydrogenating the product obtained to form a compound of formula I in which R_2 is alkyl having 1—10 C atoms, or, when X is H, OH, successively splitting off water from and hydrogenating the compound of formula III to form a compound of formula I in which R_2 is H, or, when X is H, OH, etherifying or esterifying the compound of formula III to form a compound of formula I in which R_2 is alkoxy or alkanoyloxy, each having 1—10 C atoms, or, when X is H, OH, chlorinating or brominating th compound of formula III to form a compound of formula I in which R_2 is Cl or Br, and, if desired, reacting said compound of formula I or a sulphonate of a compound of formula III in which X is H, OH, with a metal cyanide to form a compound of formula I in which R_2 is CN.

9. A process for the preparation of a perhydrophenanthrene derivative of formula I specified in Claim 1, substantially as herein described in any of Examples 1—134.

10. A liquid crystalline dielectric for electro-optic display elements, which comprises at least one perhydrophenanthrene derivative of formula I specified in Claim 1.

11. A liquid crystalline dielectric substantially as herein described in any of Examples A to D.

12. An electro-optical display element comprising a liquid crystal cell, the cell containing a liquid crystalline dielectric according to Claim 10 or 11.

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